



On-Board Chemical Propulsion Technology

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Abstract

On-board propulsion technology is critical in meeting the mission needs of the NASA enterprises, as well as those from other government agencies and industry. On-board propulsion functions include orbit insertion, orbit maintenance, constellation maintenance, precision positioning, in-space maneuvering, de-orbiting, vehicle reaction control, planetary retro, and planetary descent/ascent. These varied propulsion functions are met by an array of small chemical and electric propulsion technologies. This paper discusses on-board chemical propulsion technology, including bipropellants, monopropellants, and micropropulsion. Bipropellant propulsion has focused on maximizing the performance of the current state-of-art Earth storable propellants by using high-temperature, oxidation-resistant chamber materials. The performance of bipropellant systems can be increased further, by operating at elevated chamber pressures and/or using higher energy oxidizers. Both options present system level difficulties for spacecraft, however. High-pressure operations will require the use of pumps introducing added mass and a level of system complexity usually avoided in spacecraft. The high-energy oxidizers options are cryogenic, which present potential storage problems for spacecraft operating over years. Furthermore, since most of the high-performance bipropellant combinations are non-hypergolic, reliable, low-power ignition systems need to be developed. Monopropellant research has focused on mixtures composed of an aqueous solution of hydroxylammonium nitrate (HAN) and a fuel component. HAN-based monopropellants, then, represent a family of propellants, who generically have higher densities and lower freezing points than the state-of-art hydrazine. HAN-based monopropellants, unlike hydrazine, do not present a vapor hazard and do not require extraordinary procedures for storage, handling, and disposal. Depending on the water content and fuel component, HAN-based monopropellant performance can be as much as 20 percent greater than hydrazine. These high-performance monopropellants, however, have an aggressive, high-temperature combustion environment and require advances in catalyst materials or suitable non-catalytic ignition options. The objective of the micropropulsion technology area is to develop low-cost, high-utility propulsion systems for the range of miniature spacecraft and precision propulsion applications.

Introduction

On-board propulsion technology is critical in meeting the mission needs of the NASA enterprises, as well as those from other government agencies, academia, and industry. On-board propulsion functions include orbit insertion, orbit maintenance, constellation maintenance, precision positioning, in-space maneuvering, de-orbiting, vehicle reaction control, planetary injection, and planetary descent/ascent. An array of electric and chemical propulsion technologies are needed to meet the differing demands of in-space applications.¹ Electric propulsion is increasing its role in satellite stationkeeping and planetary spacecraft primary propulsion. On-board chemical propulsion is still necessary for high-thrust (relative to electric propulsion), short-duration, and/or power-limited applications. NASA Glenn Research Center (GRC) has maintained a sustained effort in on-board chemical propulsion, with the goal of advancing the state-of-art (SOA) and increasing the understanding of the monopropellant, bipropellant, and micropropulsion technology areas. This paper discusses on-board chemical propulsion technology with an emphasis on activities conducted or sponsored by NASA GRC.

Bipropellant Technology

The bipropellant technology area is illustrated in figure 1. Earth storable (amine) propellants, operating at nominal 690 kPa chamber pressures, represent the current SOA in bipropellant technology. Bipropellant propulsion systems using monomethylhydrazine (MMH)/nitrogen tetroxide (NTO) have been used extensively in planetary spacecraft for primary propulsion. MMH/NTO engines are also used for orbit insertion and orbit maintenance of satellites, as well as in the auxiliary propulsion systems of the Shuttle Orbiter. Hydrazine (N₂H₄)/NTO is another Earth storable combination that is commonly used in satellite propulsion. N₂H₄/NTO can be used in “dual mode” propulsion system, where the bipropellant is used for primary propulsion and N₂H₄ is used for auxiliary propulsion in monopropellant, arcjet, or electrothermal engines. Earth storable bipropellants have advantages in being hypergolic (thus not requiring an ignition system) and ambient-temperature liquids (thus not requiring extensive thermal management, aside for heaters to prevent freezing).

Until recently the performance of Earth storable bipropellants was limited by the thermal limits of the disilicide-coated C103 chamber materials. The development of iridium-coated rhenium (Ir/Re) chamber materials has raised the thermal margin from 1370 to 2200 °C, effectively allowing the maximum performance of Earth storable engines operating at conventional chamber pressures.^{2,3} A 445-N class, NTO/MMH engine with a specific impulse (Isp) of 324 sec has flown on commercial satellites.⁴ Flight, 445-N class, NTO/N₂H₄ engines have been qualified, achieving an Isp ≥ 328 sec.^{5,6}

The performance of Earth storable engines can be increased further by operating at elevated chamber pressures. In a technology effort in the mid-1990's, stable combustion of 222- and 445-N class engines, operating on NTO/MMH and NTO/N₂H₄, was demonstrated at chamber pressures up to 4.2 MPa.^{7,8} The additional heat flux of operating small engines at elevated pressure was handled by the use of high-temperature chamber materials (Ir/Re). At 3.5 MPa chamber pressure, NTO/MMH demonstrated an Isp of 335 sec and NTO/N₂H₄ had an Isp of 338 sec. This did not necessarily represent the upper limit of performance at this elevated chamber pressure.

Operation at elevated chamber pressures, however, has a significant system impact. Pressure-fed systems are preferred in spacecraft because of simplicity and reliability. The increased pressurant mass and, to a lesser extent, pressurant tank mass detracts from much of the mass benefit gained by the performance increase. Incorporation of pumps will avoid the negative pressurant mass impact, but will also introduce complexity and/or additional power requirements into the system. Because of these system-level concerns, the high-pressure Earth storable bipropellant technology effort ended before flighttype engines were tested. The same issues about high-pressure operation are applicable to other bipropellant combinations. High-pressure operation will raise Isp, but spacecraft-appropriate pump technology would need to be developed to benefit from the increased performance.

Using a more energetic oxidizer than NTO can also increase bipropellant performance. With the exception of hydrogen (H₂), the oxidizer will have a more significant impact on Isp performance than the fuel. This is not to say that different fuels would not be considered for issues related to density, compatibility, ignition, or toxicity. Liquid oxygen (LOX) represents a more energetic oxidizer than the amine options. Although LOX can be considered a space storable (boiling point = 90 K), even a mild cryogen has never been used in a planetary spacecraft propulsion system, which require years of storage. The preference would be for passive storage, since the addition of a thermodynamic vent or an active cooling system would add complexity and mass to the system. Also, there is pressurant mass penalty for using an ambient-temperature gas to pressurize a cryogenic propellant. In the mid-1990's, a technology effort demonstrated 354 sec Isp on LOX/N₂H₄ propellants in an 890-N engine, operating at 1380 kPa.⁹ The effort was oriented toward satellite propulsion efforts. Because of concerns about incorporating a cryogen in a satellite propulsion system, the effort never progressed to development of flight hardware.

Fluorinated oxidizers represent the highest level of performance for oxidizers. Fluorine (F₂) is the highest performing option, but is a mild cryogen (boiling point = 85 K) and has considerations in terms of material compatibility and toxicity. Oxygen difluoride (OF₂) is an even milder cryogen (boiling point = 128 K) with less compatibility concerns, but is even more toxic than F₂. Despite these issues, the appeal of fluorinated oxidizers is Isp performance from 380 to 390 sec with N₂H₄. There was testing with these oxidizers in the 1970's¹⁰ and more recently there has been an investigation in resurrecting the technology.¹¹

H₂ can be used with LOX or F₂ to provide the highest Isp performance of any bipropellant combination (short of using exotic, undeveloped chemicals). Isp performance well above 400 sec is possible with O₂/H₂ and F₂/H₂. However, H₂ is a very deep cryogen (boiling point = 20 K) and would require an active cooling system. A review of low-thrust O₂/H₂ engine development can be found in reference 12. A description of F₂/H₂ engine testing can be found in reference 13.

There are other bipropellant options, where increased Isp performance may be achieved, but other mission drivers may be more important. For reusable and/or manned applications, the use of non-toxic propellants will save ground processing costs and increase safety. Although O₂/H₂ has been proposed for these applications in the past,¹⁴ development efforts have more recently focused on O₂/ethanol systems.¹⁵ The use of hydrogen peroxide (H₂O₂) as an oxidizer with a hydrocarbon fuel has also been considered for non-toxic applications.¹⁶

Increased density is an important consideration for some applications. Chlorine pentafluoride (ClF₅) is 23% denser than NTO (though with similar toxicity considerations). ClF₅ was investigated as an oxidizer for divert propulsion programs in the 1990's.¹⁷ Adding gelling agents to propellants can increase their density and Isp performance. There has been use of gelled propellants in tactical applications¹⁸ and have been investigated for larger thrust applications.¹⁹

There has been recent testing using NTO with an increased amount of mixed oxides of nitrogen. The references to NTO in this paper have actually referred to a NTO mixture with 3% mixed oxides of nitrogen (MON-3). The freezing point of NTO can be depressed from 258 to 219 K by the addition of 25% mixed oxides of nitrogen (MON-25). The low freezing point oxidizer could be used with little or no thermal control (and its associated power requirements), such as in Mars atmospheric applications. Recently testing was conducted with MON-25/MMH propellants, using existing NTO/MMH engines.^{20,21} The testing demonstrated that there was no significant degradation of performance using the MON-25 oxidizer.

Water-based propulsion systems would use electrolyzers to generate gaseous H₂ and gaseous O₂ from water. The gaseous propellants can be used for propulsion and for power generation in fuel cells, which would produce water as a byproduct. Water-based propulsion was the original baseline for space station propulsion²² and had been proposed in the 1970's²³ and more recently²⁴ for satellite systems.

Monopropellant Technology

The monopropellant technology area is illustrated in figure 2. Catalytic-decomposed N₂H₄ has been the SOA of monopropellant technology for spacecraft for the past three decades. Shell 405, developed in the 1960's, spontaneously decomposes N₂H₄, allowing for a reliable ignition system. Monopropellant N₂H₄ has been used extensively for spacecraft and expendable launch vehicle attitude control and primary propulsion for smaller spacecraft, as well as for gas generator applications. H₂O₂ has also been used as a monopropellant in the past, though it is lower performing than N₂H₄.

Since the late 1990's, there have been NASA-sponsored efforts to develop high-performance, non-toxic monopropellant systems. The goal is to develop monopropellant propulsion systems with significantly better performance, thermal, and hazard properties than monopropellant N_2H_4 . The technology efforts have focused on a family of monopropellant formulations consisting of an aqueous solution of hydroxylammonium nitrate (HAN), which serves as the oxidizer, and a fuel component. HAN usually composes the majority of the formulation and dominates the characteristics of the monopropellant. Generically, HAN-based monopropellants are at least 40 percent denser than N_2H_4 , have freezing points less than 0°C , have no vapor hazard, and do not require any extraordinary storage, handling, or disposal procedures. The selection of the fuel component and relative percentage of HAN, fuel, and water determine the combustion temperature and, therefore, performance.

HAN-based monopropellants have their genesis in an Army program to develop liquid gun propellants (LGP) as insensitive munitions.²⁵ The most developed LGP formulation was XM46, which used triethanolammonium nitrate (TEAN) as the fuel component. However, in rocket testing, XM46 did not provide acceptable combustion characteristics at pressures less than 3.5 MPa.²⁶ For spacecraft applications, other fuel components would have to be used, although LGP's could still be pursued for larger thrust applications, such as third stages.

When the monopropellant technology effort started, there was a formidable challenge in adapting a class of propellants originally developed as munitions for large guns (operated at 350 MPa) for use in satellite propulsion systems (operating less than 2.8 MPa). Since HAN-based monopropellants are actually mixtures of an aqueous oxidizer and a fuel, its decomposition and combustion is much more complex than single molecular entities such as N_2H_4 or H_2O_2 . HAN first decomposes into hydroxyl amine and nitric acid, which then reacts with the fuel. The decomposition process and burning behavior is not well understood for HAN-based monopropellants.

The decomposition and combustion environment for HAN-based monopropellants is harsh. Because the molecular weight of its exhaust products are higher than in N_2H_4 systems, HAN-based monopropellants must operate at higher temperatures to achieve the same performance. The decomposition process produces nitric acid as a combustion intermediate. The combustion products include steam and carbon dioxide. The current SOA monopropellant catalyst (Shell 405) cannot withstand this high-temperature, corrosive decomposition environment for the lifetimes needed for most spacecraft applications (multiple hours).

In the late 1990's, a HAN-monopropellant technology effort focused on larger thrust applications, using the LGP formulations. A successful firing (using a pyrotechnic ignition system) of a heavyweight engine was achieved, running a formulation (LGP 1898) that used diethylhydroxylammonium nitrate (DEHAN) as the fuel. The engine operated up to a chamber pressure of 4.8 MPa and was projected to have an Isp of 270 sec (at 50:1 area ratio).²⁷

Another effort, also in the late 1990's, screened several candidate fuels in laboratory and combustion testing.²⁸ The properties, storage stability, and combustion behavior of several resultant formulations were characterized.²⁹ In the initial development, it was decided to focus on a formulation compatible with SOA catalysts. This meant the formulation would have a lower Isp than N_2H_4 , though it would still provide a volume benefit. This approach would allow focus on propellant and thruster development, without simultaneously entering a lengthy catalyst material development effort. Furthermore, even this "low-temperature" HAN formulation would provide ground processing and volume benefits that would be important to small satellite users.

A formulation (HAN204GLY) using glycine as a fuel and excess water to keep combustion temperatures down to 1100 °C was selected for development. This resulted in a projected delivered Isp of 190 sec for the formulation (93% of the theoretical Isp of 204 sec). A storage stability issue for the HAN204GLY blend was addressed by the addition of stabilizers that provided for long-term storage (years) at temperatures up to 65 °C.²⁹ The stabilized version of HAN204GLY did not differ in combustion performance from the unstabilized version. A 4.5-N, HAN thruster was designed and different active metals, bed configurations, and injector designs were tested.^{30,31} The 4.5-N thruster, using the HAN204GLY blend, was tested to a duty cycle appropriate for orbit insertion of a 20-kg satellite. The thruster accumulated over 8000 seconds of operation, firing primarily in steady-state mode. The thruster was operated in blowdown mode to simulate a satellite propulsion system. There was approximately 7.5% degradation in chamber pressure (and therefore, thrust) from the first to last test (conducted at the same feed pressure). Pulse testing was also conducted, though the use of a facility valve affected impulse bit repeatability.

Recent efforts have turned toward formulations with $I_{sp} \geq 250$ sec. Assuming combustion efficiencies of 93%, this suggested formulations with theoretical $I_{sp} \geq 270$ sec. A formulation that uses methanol as the fuel component (HAN269MEO) was designated as the baseline. The effects of varying stoichiometry (i.e., oxidizer-rich and fuel-rich blends were tested) were investigated.³²

The combustion temperatures of these formulations are beyond the capability of Shell 405 for more than minutes of life. Testing with Shell 405 or similar catalysts successfully induced combustion, but with a catalyst life on the order of a couple of minutes. The catalyst carrier material would shrink, leaving voids in the catalyst bed. These voids would allow propellant to pool inside the reactor and combust randomly, leading to undesirable combustion pressure roughness and pressure spikes. To operate in the aggressive combustion environment of HAN-based monopropellants, the carrier materials cannot be susceptible to shrinkage over the temperature range and the active metal cannot melt or evaporate at high temperature (at least 1700 K).

For similar reasons of high-temperature and corrosive combustion products, advanced materials are needed for the catalytic reactor and thruster walls. Ir/Re is the state-of-art of high-temperature, oxidation-resistant chamber materials for high-performance Earth storable engines. The life of Ir/Re under the HAN combustion environment, however, has not been demonstrated.

The Pennsylvania State University (under a NASA grant) is conducting combustion experiments with HAN-based monopropellants to better understand its decomposition mechanisms and burning behavior. This work has generated burn rate data and insight to HAN combustion processes for HAN-glycine³³ and HAN-methanol³⁴ formulations.

The majority of HAN compatibility work has been done in the liquid gun propellant programs with XM46. Despite these efforts the HAN compatibility database is far from complete and sometimes unclear, because of differing ways of conducting tests and interpreting results. There are efforts underway to better define the material compatibility database for HAN-based monopropellants.³⁵ It is known that HAN is not compatible with silica-containing materials, such as the state-of-art tank bladder elastomer. Finding a suitable tank design, using either a compatible elastomer material for the bladder or an alternative delivery system, is critical in implementing HAN-based monopropellant systems.

Chemical Micropropulsion Technology

Reducing the size of spacecraft is a desirable goal for some applications, as it can lead to the use of cheaper launch vehicles and provide for different approaches to accomplish missions (such as the use of satellite constellations). “Nanosatellites”, spacecraft in the 10- to 20-kg range, are being developed for a constellation demonstration mission.³⁶ There are more ambitious efforts to develop spacecraft less than

10-kg, employing micro-electricalmechanical systems (MEMS) fabrication technology.³⁷ At some point, simply miniaturizing propulsion subsystems becomes untenable. Figure 3 illustrates this point in terms of spacecraft power and mass (the implications for the volume envelope are even more severe). This is due to the reality that all current spacecraft propulsion systems have a lower weight/size limit below which performance suffers substantially as the result of losses associated with the smallness of physical size (incomplete combustion, wall heat loss, and shear layer losses). At this point reduced-scale versions of conventional systems will no longer be practical and a fundamentally different approach to propulsion must be taken.³⁸

There are several on-going efforts to develop miniature propulsion systems, including chemical and electric propulsion concepts.³⁹⁻⁴¹ Many of these concepts are tailored for MEMS-scale spacecraft applications, but micropropulsion has applications as compact, precision propulsion systems for “small satellites” (defined by NASA as being in the 40- to 100-kg size range). Propulsion functions for small satellites include spin-up and spin-down, precision positioning and pointing, constellation maintenance, and deorbiting. Grouping micropropulsion systems in arrays will allow their use for larger thrust applications. These “macroscale” functions of micropropulsion may be the nearer term application.

GRC had been developing a valveless, flexible micropropulsion concept that would use an array of MEMS thruster units, arranged in the configuration best suited for a particular application. Different thruster sizes (throat areas, nozzle area ratios) would provide for a range of thrust levels (from μN 's to mN 's) within the same array. Several thrusters could be fired simultaneously for thrust levels higher than the basic units, or in a rapid sequence in order to provide gradual but steady low-g acceleration. Decomposing solid propellant pellets (slow-burning propellants also referred to as gas generators) would be used, providing long-term, leak-free storage. Initiation of the propellants would be accomplished with a diode laser-based, fiber-optic network. Silicon is transparent at wavelengths above 1.3 microns, allowing laser penetration and initiation without structure-compromising feedthroughs. Power requirements for initiation would be less than 100 milliwatts. GRC conducted initial testing involving the decomposition of a high nitrogen compound and diode laser initiation.⁴²

The optimization of rectangular nozzles, subjected to low Reynolds number, viscous-dominated flows is an issue. There have been experimental and computational efforts investigating the performance of miniature nozzles.^{43,44} Established approaches to optimization of nozzles breakdown at lower Reynolds numbers, where viscous effects begin to become more prevalent. At the miniature scale, the predominance of viscous effects is amplified. Furthermore, the nature of the MEMS manufacturing process results in rectangular rather than circular nozzles. Depending on the aspect ratio of the nozzle, the top and bottom wall boundaries are likely to heavily influence the flowfield behavior. These physical differences of nozzles at the miniature scale indicate a different optimization of performance. Under a NASA grant at the Pennsylvania State University, numerical modeling of miniature, rectangular nozzles has been conducted using Direct Simulation Monte Carlo (DSMC). Modeling was extended from two-dimensional to three-dimensional geometries⁴⁵ and extended to couple wall thermal effects to fluid flow.⁴⁶

Testing has been conducted of flat micronozzles under ambient-temperature nitrogen and helium flows.⁴⁷ This testing, in conjunction with numerical modeling, has indicated that a short area ratio will provide the best performance for micronozzles. Testing with nitrogen showed a performance peak around area ratio 5, which is consistent with computational modeling that has been conducted. Testing with helium flows showed performance peaking at area ratio 1.5, suggesting that no nozzles might be best for these flows. Testing with ambient-temperature flows in flat, rectangular micronozzles are the first step to understanding nozzle optimization at this scale. More testing will be conducted to understand the influence of throat area (small throat widths), throat aspect ratio (larger depths), and gas temperature (heated flows) on the performance of these non-optimized nozzles.

GRC has also supported technology efforts to develop a challenging MEMS propulsion technology. Developed by the Massachusetts Institute of Technology (MIT), MEMS fabrication methods would be used to produce liquid bipropellant engines on a silicon wafer.⁴⁸ The “microrocket” could be pressure-fed or the concept can be extended to a pump-fed, regeneratively-cooled engine, utilizing planar, MEMS turbomachinery. Although the throats of these microrockets would be on the order of 100 microns wide, they would operate at chamber pressures above 100 atm, providing 15 N of thrust. The microrockets would be clustered together to provide higher thrust levels. Considering their small size and their batch-fabricated manufacture, hundreds or even thousands of MEMS thrusters could be clustered on a panel with minimal impact to mass, volume, or production costs.

Summary

To meet the varying needs of spacecraft/satellite propulsion applications, a range of on-board propulsion technologies are used. The on-board chemical propulsion area includes bipropellant, monopropellant, and micropropulsion technologies. Bipropellant performance can be increased by using more energetic propellants and/or operating at higher chamber pressures. There are also other drivers, such as toxicity, high-density storage, or low-freezing-point propellants, which would suggest other bipropellant combinations. Monopropellant performance can be increased by using formulations composed of an aqueous solution of HAN and a fuel component. Chemical micropropulsion technologies can be used for precision propulsion needs as well as for MEMS spacecraft application.

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Bipropellant Technology

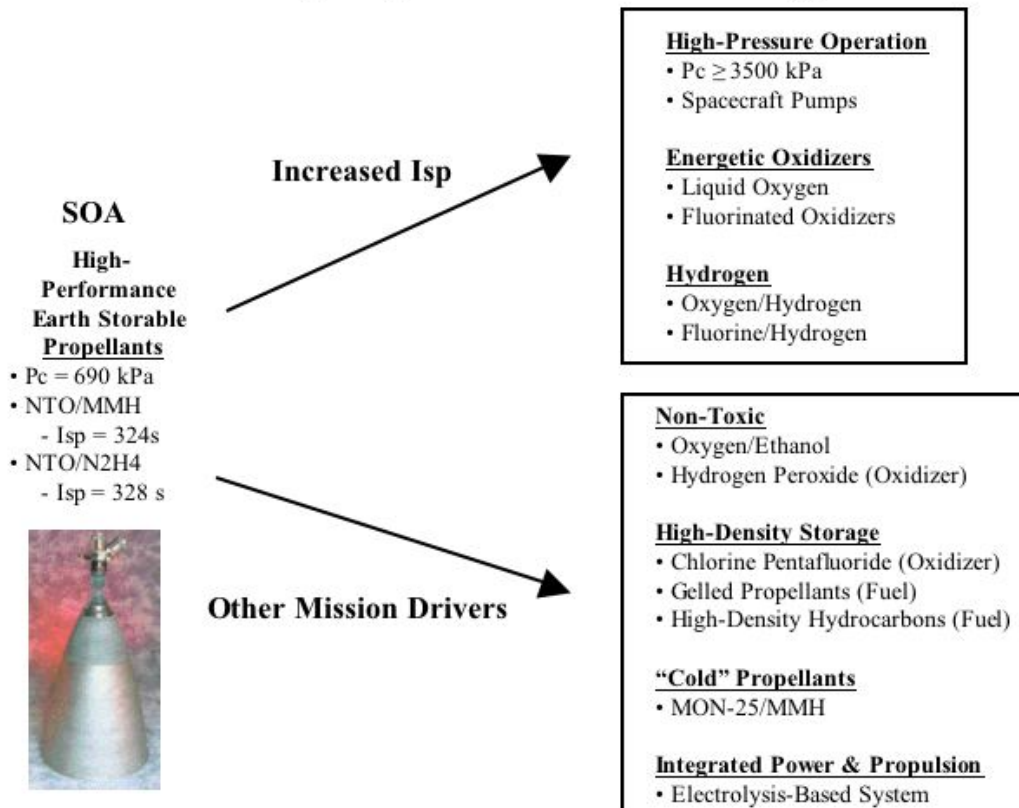


Figure 1: Bipropellant technology area

Monopropellant Technology

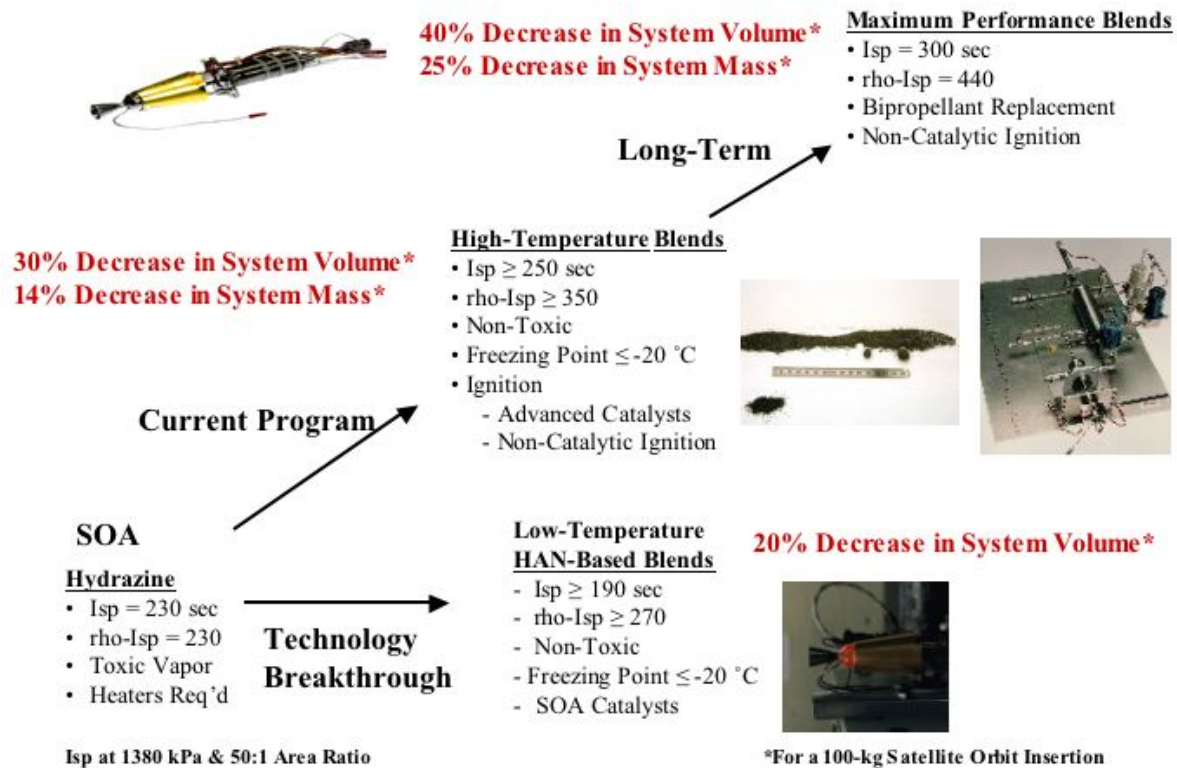


Figure 2: Monopropellant technology area

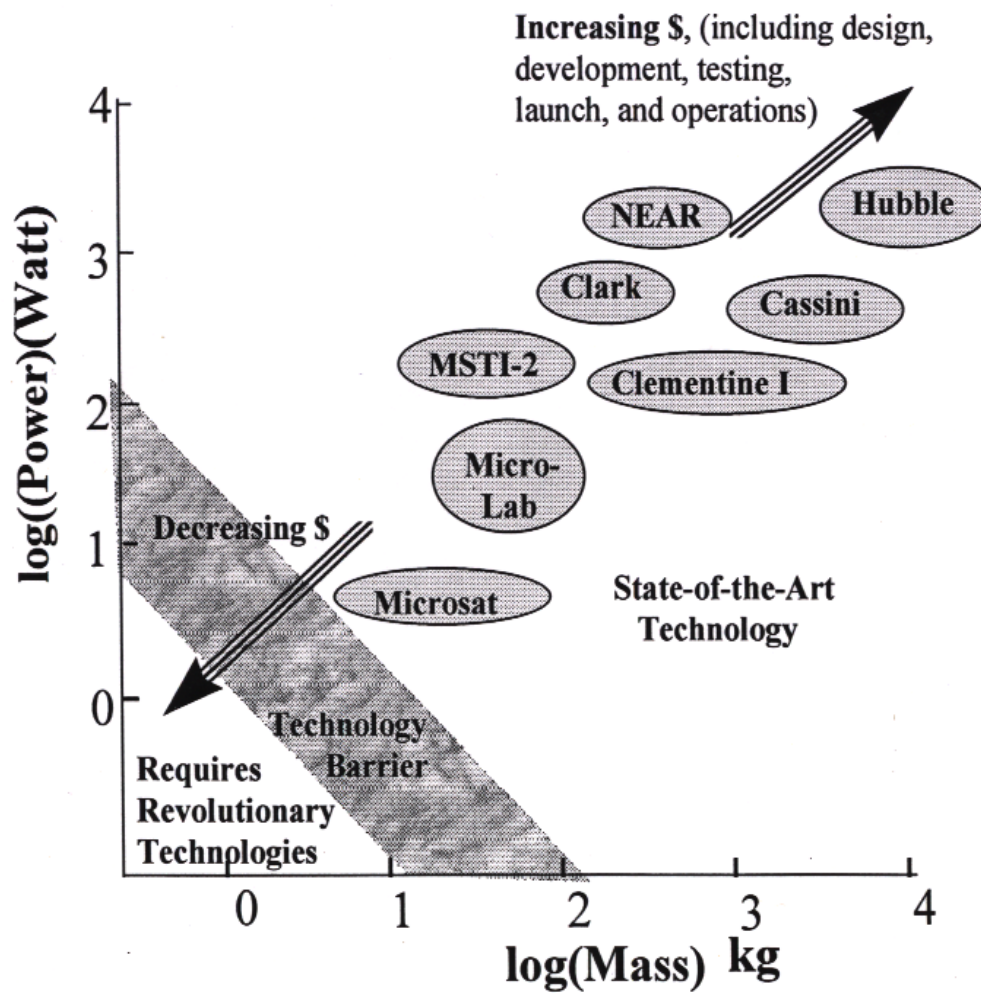


Figure 3: Need for micropropulsion

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| 13. ABSTRACT (Maximum 200 words) On-board propulsion functions include orbit insertion, orbit maintenance, constellation maintenance, precision positioning, in-space maneuvering, de-orbiting, vehicle reaction control, planetary retro, and planetary descent/ascent. This paper discusses on-board chemical propulsion technology, including bipropellants, monopropellants, and micropropulsion. Bipropellant propulsion has focused on maximizing the performance of Earth storable propellants by using high-temperature, oxidation-resistant chamber materials. The performance of bipropellant systems can be increased further, by operating at elevated chamber pressures and/or using higher energy oxidizers. Both options present system level difficulties for spacecraft, however. Monopropellant research has focused on mixtures composed of an aqueous solution of hydroxylammonium nitrate (HAN) and a fuel component. HAN-based monopropellants, unlike hydrazine, do not present a vapor hazard and do not require extraordinary procedures for storage, handling, and disposal. HAN-based monopropellants generically have higher densities and lower freezing points than the state-of-art hydrazine and can higher performance, depending on the formulation. High-performance HAN-based monopropellants, however, have aggressive, high-temperature combustion environments and require advances in catalyst materials or suitable non-catalytic ignition options. The objective of the micropropulsion technology area is to develop low-cost, high-utility propulsion systems for the range of miniature spacecraft and precision propulsion applications. | | | | |
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